

BEST AVAILABLE COPY

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



5

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification 4 :</b> C07C 55/00, 69/34 C07D 307/34, C10M 129/93 C10L 1/18, 1/22		<b>A1</b>	<b>(11) International Publication Number:</b> WO 90/03359 <b>(43) International Publication Date:</b> 5 April 1990 (05.04.90)		
<b>(21) International Application Number:</b> PCT/US89/04270 <b>(22) International Filing Date:</b> 29 September 1989 (29.09.89)		<b>(81) Designated States:</b> AT (European patent), AU, BE (European patent), BR, CH (European patent), DE (European patent), DK, FI, FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent).			
<b>(30) Priority data:</b> 251,613 29 September 1988 (29.09.88) US		<b>Published</b> <i>With international search report.</i>			
<b>(71) Applicant:</b> CHEVRON RESEARCH COMPANY [US/US]; P.O. BOX 7141, San Francisco, CA 94120-7141 (US).					
<b>(72) Inventor:</b> HARRISON, James, J. ; 12 Stonehaven Court, Novato, CA 94947 (US).					
<b>(74) Agents:</b> CAROLI, Claude, J. et al.; Chevron Corporation, Law Department, P.O. Box 7141, San Francisco, CA 94120-7141 (US).					
<b>(54) Title:</b> NOVEL POLYMERIC DISPERSANTS HAVING ALTERNATING POLYALKYLENE AND SUCCINIC GROUPS					
<b>(57) Abstract</b> <p>Novel copolymers of unsaturated acidic reactants and high molecular weight olefins wherein at least 20 percent of the total high molecular weight olefin comprises the alkylvinylidene isomer are useful as dispersants in lubricating oils and fuels and also may be used to prepare polysuccinimides and other post-treated additives useful in lubricating oils and fuels.</p>					

***FOR THE PURPOSES OF INFORMATION ONLY***

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MR	Mauritania
BE	Belgium	GA	Gabon	MW	Malawi
BF	Burkina Faso	GB	United Kingdom	NL	Netherlands
BG	Bulgaria	HU	Hungary	NO	Norway
BJ	Benin	IT	Italy	RO	Romania
BR	Brazil	JP	Japan	SD	Sudan
CA	Canada	KP	Democratic People's Republic of Korea	SE	Sweden
CF	Central African Republic	KR	Republic of Korea	SN	Senegal
CG	Congo	LJ	Liechtenstein	SU	Soviet Union
CH	Switzerland	LK	Sri Lanka	TD	Chad
CM	Cameroon	LU	Luxembourg	TG	Togo
DE	Germany, Federal Republic of	MC	Monaco	US	United States of America
DK	Denmark				

1

01           NOVEL POLYMERIC DISPERSANTS HAVING ALTERNATING  
02           POLYALKYLENE AND SUCCINIC GROUPS

03

04           BACKGROUND OF THE INVENTION

05

06       The present invention relates to compositions which are  
07       useful as intermediates for dispersants used in lubricating  
08       oil compositions or as dispersants themselves. In addition,  
09       some of these compositions are useful in the preparation of  
10       novel high molecular weight dispersants which have superior  
11       dispersant properties for dispersing sludge and varnish and  
12       superior Viton Seal compatibility.

13

14       The high molecular weight dispersants of the present  
15       invention also advantageously impart fluidity modifying  
16       properties to lubricating oil compositions which are suffi-  
17       cient to .  
18       index improver from multigrade lubricating oil compositions  
19       which contain these dispersants.

20

21       Alkenyl-substituted succinic anhydrides have been used as  
22       dispersants. Such alkenyl-substituted succinic anhydrides  
23       have been prepared by two different processes, a thermal  
24       process (see, e.g., U.S. Patent No. 3,361,673) and a  
25       chlorination process (see, e.g., U.S. Patent No. 3,172,892).  
26       The polyisobutetyl succinic anhydride ("PIBSA") produced by  
27       the thermal process has been characterized as a monomer  
28       containing a double bond in the product. Although the exact  
29       structure of chlorination PIBSA has not been definitively  
30       determined, the chlorination process PIBAs have been charac-  
31       terized as monomers containing either a double bond, a ring,  
32       other than a succinic anhydride ring and/or chlorine in the  
33       product. (See J. Weill and B. Sillion, "Reaction of  
34       Chlorinated Polyisobutene with Maleic Anhydride: Mechanism

01   Catalysis by Dichloromaleic Anhydride", Revue de l'Institut  
02   Français du Pétrole, Vol. 40, No. 1, pp. 77-89  
03   (January-February, 1985).] Such compositions include  
04   one-to-one monomeric adducts (see, e.g., U.S. Patents  
05   Nos. 3,219,666; 3,381,022) as well as adducts having poly-  
06   alkenyl-derived substituents adducted with at least 1.3  
07   succinic groups per polyalkenyl-derived substituent (see,  
08   e.g., U.S. Patent No. 4,234,435).

09

10 In addition, copolymers of maleic anhydrides and some ali-  
11 phatic alpha-olefins have been prepared. The polymers so  
12 produced were useful for a variety of purposes including  
13 dispersants for pigments and intermediates in the prepara-  
14 tion of polyesters by their reaction with polyols or poly-  
15 epoxides. However, olefins having more than about 30 carbon  
16 atoms were found to be relatively unreactive. (See, e.g.,  
17 U.S. Patents Nos. 3,451,100; 3,550,455; 3,550,456;  
18 3,560,457; 3,580,893; 3,706,704; 3,729,450; and 3,729,451).

19

## **SUMMARY OF THE INVENTION**

21

22 The present invention is directed to novel compositions  
23 useful as additives which comprise copolymers of an unsatu-  
24 rated acidic reactant and high molecular weight olefin  
25 wherein at least about 20 percent of the total high  
26 molecular weight olefin comprises the alkylvinylidene  
27 isomer, said copolymers having alternating succinic and  
28 polyalkyl groups. The high molecular weight olefin has a  
29 sufficient number of carbon atoms such that the resulting  
30 copolymer is soluble in lubricating oil. Suitable olefins  
31 include those having about 32 carbon atoms or more (prefer-  
32 ably having about 52 carbon atoms or more). Those preferred  
33 high molecular weight olefins include polyisobutenes.  
34 Especially preferred are polyisobutenes having average

3

01 molecular weights of from about 500 to about 5000 and in  
02 which the alkylvinylidene isomer comprises at least 50  
03 percent of the total olefin.

04

05 These copolymers are useful as dispersants themselves and  
06 also as intermediates in the preparation of other dispersant  
07 additives having improved dispersancy and/or detergency  
08 properties when employed in a lubricating oil.

09

10 These copolymers are also advantageous because they do not  
11 contain double bonds, rings, other than succinic anhydride  
12 rings, or chlorine (in contrast to thermal and chlorination  
13 PIBSAs) and as such have improved stability, as well as  
14 improved environmental properties due to the absence of  
15 chlorine.

16

17 The present invention is also directed to polysuccinimides  
18 which are prepared by reacting a copolymer of the present  
19 invention with a polyamine to give a polysuccinimide. The  
20 present invention is directed to mono-polysuccinimides  
21 (where a polyamine component reacts with one succinic  
22 group); bis-polysuccinimides (where a polyamine component  
23 reacts with a succinic group from each of two copolymer  
24 molecules, thus effectively cross-linking the copolymer  
25 molecules); and higher polysuccinimides (where a polyamine  
26 component reacts with a succinic group from each of greater  
27 than 2 copolymer molecules). These polysuccinimides are  
28 useful as dispersants and/or detergents in fuels and oils.  
29 In addition, these polysuccinimides have advantageous vis-  
30 cosity modifying properties, and may provide a viscosity  
31 index credit ("V.I. Credit") when used in lubricating oils,  
32 which may permit elimination of some portion of viscosity  
33 index improver ("V.I. Improver") from multigrade lubricating  
34 oils containing the same.

4

01 In addition, the polysuccinimides of the present invention  
02 can form a ladder polymeric structure or a cross-linked  
03 polymeric structure. These structures are advantageous  
04 because it is believed such structures are more stable and  
05 resistant to hydrolytic degradation and also to degradation  
06 by shear stress.

07

08 In addition, the present invention is directed to modified  
09 polysuccinimides wherein one or more of the nitrogens of the  
10 polyamine component is substituted with a hydrocarbyl oxy-  
11 carbonyl, a hydroxyhydrocarbyl oxycarbonyl or a hydroxy  
12 poly(oxyalkylene)-oxycarbonyl. These modified polysuccini-  
13 mides are improved dispersants and/or detergents for use in  
14 fuels or oils.

15

16 Accordingly, the present invention also relates to a lubri-  
17 cating oil composition comprising a major amount of an oil  
18 of lubricating viscosity and an amount of a copolymer,  
19 polysuccinimide or modified succinimide additive of the  
20 present invention sufficient to provide dispersancy and/or  
21 detergency. The additives of the present invention may also  
22 be formulated in lubricating oil concentrates which comprise  
23 from about 90 to about 50 weight percent of an oil of lubri-  
24 cating viscosity and from about 10 to about 50 weight  
25 percent of an additive of the present invention.

26

27 Another composition aspect of the present invention is a  
28 fuel composition comprising a major portion of a fuel  
29 boiling in a gasoline or diesel range and an amount of  
30 copolymer, polysuccinimide or modified succinimide additives  
31 sufficient to provide dispersancy and/or detergency. The  
32 present invention is also directed to fuel concentrates  
33 comprising an inert stable oleophilic organic solvent  
34 boiling in the range of about 150°F to about 400°F and from

01 about 5 to about 50 weight percent of an additive of the  
02 present invention.

03

## 04 Definitions

05

06 As used herein, the following terms have the following  
07 meanings unless expressly stated to the contrary.

08

09 The term "unsaturated acidic reactants" refers to maleic or  
10 fumaric reactants of the general formula:

11

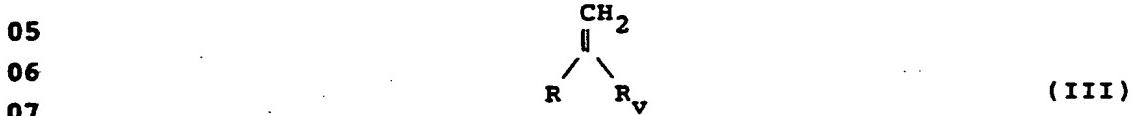


wherein X and X' are the same or different, provided that at least one of X and X' is a group that is capable of reacting to esterify alcohols, form amides or amine salts with ammonia or amines, form metal salts with reactive metals or basically reacting metal compounds and otherwise function as acylating agents. Typically, X and/or X' is -OH, -O-hydrocarbyl, -OM<sup>+</sup> where M<sup>+</sup> represents one equivalent of a metal, ammonium or amine cation, -NH<sub>2</sub>, -Cl, -Br, and taken together X and X' can be -O- so as to form an anhydride. Preferably X and X' are such that both carboxylic functions can enter into acylation reactions. Maleic anhydride is a preferred unsaturated acidic reactant. Other suitable unsaturated acidic reactants include electron-deficient olefins such as monophenyl maleic anhydride; monomethyl, dimethyl, mono-chloro, monobromo, monofluoro, dichloro and difluoro maleic anhydride; N-phenyl maleimide and other substituted maleimides; isomaleimides; fumaric acid, maleic acid, alkyl hydrogen maleates and fumarates, dialkyl fumarates and maleates, fumaronilic acids and maleanic acids; and maleonitrile, and fumaronitrile.

6

01 The term "alkylvinylidene" or "alkylvinylidene isomer"  
02 refers to high molecular weight olefins and polyalkylene  
03 components having the following vinylidene structure

04



08 wherein R is alkyl or substituted alkyl of sufficient chain  
09 length to give the resulting molecule solubility in lubri-  
10 cating oils and fuels, thus R generally has at least about  
11 30 carbon atoms, preferably at least about 50 carbon atoms  
12 and R<sub>v</sub> is lower alkyl of about 1 to about 6 carbon atoms.  
13

14 The term "soluble in lubricating oil" refers to the ability  
15 of a material to dissolve in aliphatic and aromatic hydro-  
16 ~~such as lubricating oils or fuels in essentially all~~  
17 proportions.  
18

19 The term "high molecular weight olefins" refers to olefins  
20 (including polymerized olefins having a residual unsatura-  
21 tion) of sufficient molecular weight and chain length to  
22 lend solubility in lubricating oil to their reaction prod-  
23 ucts. Typically olefins having about 32 carbons or greater  
24 (preferably olefins having about 52 carbons or more)  
25 suffice.  
26

27 The term "high molecular weight polyalkyl" refers to poly-  
28 alkyl groups of sufficient molecular weight and hydrocarbyl  
29 chain length that the products prepared having such groups  
30 are soluble in lubricating oil. Typically these high  
31 molecular weight polyalkyl groups have at least about 30  
32 carbon atoms, preferably at least about 50 carbon atoms.  
33 These high molecular weight polyalkyl groups may be derived  
34 from high molecular weight olefins.

7

01 The term "PIBSA" is an abbreviation for polyisobutenyl  
02 succinic anhydride.

03

04 The term "polyPIBSA" refers to a class of copolymers within  
05 the scope of the present invention which are copolymers of  
06 polyisobutene and an unsaturated acidic reactant which have  
07 alternating succinic groups and polyisobutyl groups.

08 PolyPIBSA has the general formula

09

10

11

12

13

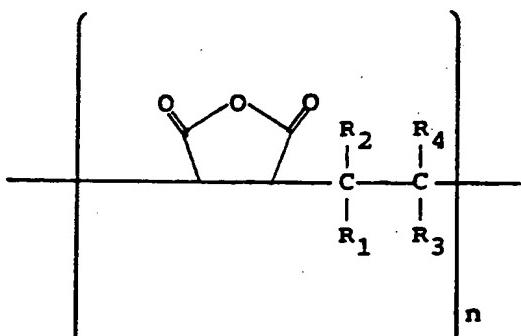
14

15

16

17

18



19 wherein n is one or greater; R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are selected from  
20 hydrogen, methyl and polyisobutyl having at least about 30 carbon  
21 atoms (preferably at least about 50 carbon atoms) wherein either  
22 R<sub>1</sub> and R<sub>2</sub> are hydrogen and one of R<sub>3</sub> and R<sub>4</sub> is methyl and the  
23 other is polyisobutyl, or R<sub>3</sub> and R<sub>4</sub> are hydrogen and one of R<sub>1</sub>  
24 and R<sub>2</sub> is methyl and the other is polyisobutyl.

25

26 The term "PIBSA number" refers to the anhydride (succinic group)  
27 content of polyPIBSA on a 100% actives basis. The PIBSA number  
28 is calculated by dividing the saponification number by the  
29 percent polyPIBSA in the product. The units are mg KOH per gram  
30 sample.

31

32

33

34

8

01 The term "succinic group" refers to a group having the formula

02

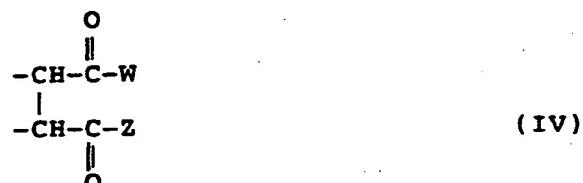
03

04

05

06

07



08 wherein W and Z are independently selected from the group  
09 consisting of -OH, -Cl, -O- lower alkyl or taken together  
10 are -O- to form a succinic anhydride group.

11

12 The term "degree of polymerization" expresses the length of  
13 a linear polymer and refers to the number of repeating  
14 (monomeric) units in the chain. The average molecular  
15 weight of a polymer is the product of the degree of polymer-  
16 ization and the average molecular weight of the repeating  
17 unit (monomer). Accordingly, the average degree of poly-  
18 merization is calculated by dividing the average molecular  
19 weight of the polymer by the average molecular weight of the  
20 repeating unit.

21

22 The term "polysuccinimide" refers to the reaction product of  
23 a copolymer of the present invention with polyamine.

24

25 BRIEF DESCRIPTION OF THE DRAWING

26

27 FIG. 1 depicts one embodiment of a polysuccinimide of the  
28 present invention, wherein R is polyisobutyl, R<sub>1</sub> is lower  
29 alkyl, I is an initiator group and T is a terminator group.

30

31

32

33

34

DETAILED DESCRIPTION OF THE INVENTION

01

02

03

04

A. COPOLYMER

05 The copolymers of the present invention are prepared by  
06 reacting a high molecular weight olefin wherein at least  
07 about 20% of the total olefin composition comprises the  
08 alkylvinylidene isomer and an unsaturated acidic reactant in  
09 the presence of a free radical initiator. Suitable high  
10 molecular weight olefins have a sufficient number of carbon  
11 atoms so that the resulting copolymer is soluble in  
12 lubricating oil and thus have on the order of about 32  
13 carbon atoms or more. Preferred high molecular weight of  
14 olefins are polyisobutenes and polypropylenes. Especially  
15 preferred are polyisobutenes, particularly preferred are  
16 those having a molecular weight of about 500 to about 5000,  
17 more preferably about 900 to about 2500. Preferred  
18 unsaturated acidic reactants include maleic anhydride.

19

20 Since the high molecular weight olefins used to prepare the  
21 copolymers of the present invention are generally mixtures  
22 of individual molecules of different molecular weights,  
23 individual copolymer molecules resulting will generally  
24 contain a mixture of high molecular weight polyalkyl groups  
25 of varying molecular weight. Also, mixtures of copolymer  
26 molecules having different degrees of polymerization will be  
27 produced.

28

29 The copolymers of the present invention have an average  
30 degree of polymerization of 1 or greater, preferably from  
31 about 1.1 to about 20, and more preferably from about 1.5 to  
32 about 10.

33

34

10

01 Among other factors, the present invention is based on my  
02 surprising finding that the reaction of these high molecular  
03 weight olefins wherein at least about 20% of the total  
04 composition comprises the methylvinylidene isomer with an  
05 unsaturated acidic reactant in the presence of a free  
06 radical initiator results in a copolymer having alternating  
07 polyalkylene and succinic groups. This is surprising in  
08 view of the teachings that reaction of polyalkenes, such as  
09 polyisobutenes, with unsaturated acidic reactants such as  
10 maleic anhydride, in the presence of a free radical  
11 initiator, resulted in a product similar to that produced by  
12 the thermal process for PIBSA which is a monomeric  
13 one-to-one adduct (see, e.g., U.S. Patent No. 3,367,864).  
14 It was taught that high molecular weight olefins were rela-  
15 tive unreactive under those conditions which was confirmed  
16 by my findings that reaction of polyisobutene prepared using  
17 ~~catalysis~~ [in which the alkylvinylidene isomer com-  
18 prised a very small proportion (less than about 10%) of the  
19 total composition] with maleic anhydride in the presence of  
20 a free radical initiator resulted in low yield of product.  
21 In addition, the product obtained was similar to thermal  
22 PIBSA in molecular weight.

23

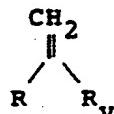
24 Thus, the copolymers of the present invention are prepared  
25 by reacting a "reactive" high molecular weight olefin in  
26 which a high proportion of unsaturation, at least about 20%  
27 is in the alkylvinylidene configuration, e.g.

28

29

30

31



32 wherein R and  $\text{R}_v$  are as previously defined in conjunction  
33 with Formula III, with an unsaturated acidic reactant in the  
34 presence of a free radical initiator. The product copolymer

01 has alternating polyalkylene and succinic groups and has an  
02 average degree of polymerization of 1 or greater.

03  
04 The copolymers of the present invention have the general  
05 formula:

06

07

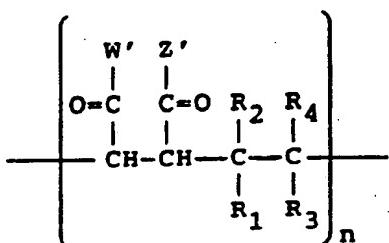
08

09

10

11

12



13

14 wherein w' and z' are independently selected from the group  
15 consisting of -OH, -O- lower alkyl or taken together are -O-  
16 to form a succinic anhydride group, n is one or greater; and  
17 w' and z' and R<sub>1</sub> and R<sub>2</sub> are selected from hydrogen, lower alkyl of  
18 1 to 6 carbon atoms, and high molecular weight polyalkyl  
19 wherein either R<sub>1</sub> and R<sub>2</sub> are hydrogen and one of R<sub>3</sub> and R<sub>4</sub>  
20 is lower alkyl and the other is high molecular weight poly  
21 alkyl, or R<sub>3</sub> and R<sub>4</sub> are hydrogen and one of R<sub>1</sub> and R<sub>2</sub> is  
22 lower alkyl and the other is high molecular weight  
23 polyalkyl.

24

25 In a preferred embodiment, when maleic anhydride is used as  
26 the unsaturated acidic reactant, the reaction produces  
27 copolymers predominately of the following formula:

28

29

30

31

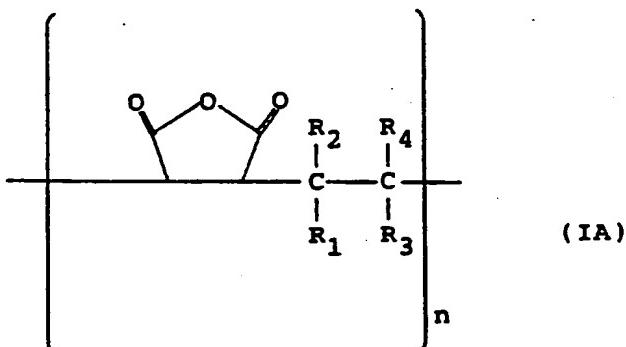
32

33

34

12

01  
02  
03  
04  
05  
06  
07  
08  
09  
10  
11



12 wherein n is about 1 to about 100, preferably about 2 to  
13 about 20, more preferably 2 to 10, and R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are  
14 selected from hydrogen, lower alkyl of about 1 to 6 carbon  
15 atoms and higher molecular weight polyalkyl, wherein either  
16 R<sub>1</sub> and R<sub>2</sub> are hydrogen and one of R<sub>3</sub> and R<sub>4</sub> is lower alkyl  
17 and the other is high molecular weight polyalkyl or R<sub>3</sub> and  
18 R<sub>4</sub> are hydrogen and one of R<sub>1</sub> and R<sub>2</sub> is lower alkyl and the  
19 other is high molecular weight polyalkyl.

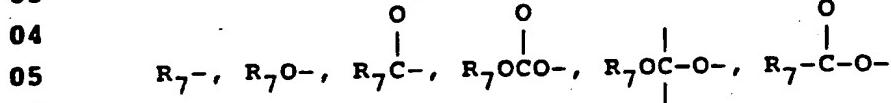
20  
21 Preferably, the high molecular weight polyalkyl group has at  
22 least about 30 carbon atoms (preferably at least about 50  
23 carbon atoms). Preferred high molecular weight polyalkyl  
24 groups include polyisobutyl groups. Preferred polyisobutyl  
25 groups include those having average molecular weights of  
26 about 500 to about 5000, more preferably from about 900 to  
27 about 2500. Preferred lower alkyl groups include methyl and  
28 ethyl; especially preferred lower alkyl groups include  
29 methyl.  
30

31 Generally, such copolymers contain an initiator group, I,  
32 and a terminator group, T, as a result of the reaction with  
33 the free radical initiator used in the polymerization  
34

13

01 reaction. In such a case, the initiator and terminator  
02 groups may be

03



6

07

where R<sub>7</sub> is hydrogen, alkyl, aryl, alkaryl, cycloalkyl, alkoxy, cycloalkoxy, acyl, alkenyl, cycloalkenyl, alkynyl; or alkyl, aryl or alkaryl optionally substituted with 1 to 4 substituents independently selected from nitrile, keto, halogen, nitro, alkyl, aryl, and the like. Alternatively, the initiator group and/or terminator group may be derived from the reaction product of the initiator with another material such as solvent; for example, the initiator may react with toluene to produce a benzyl radical.

١٧

18 The copolymers of the present invention differ from the  
19 PIBSAs prepared by the thermal process in that the thermal  
20 process products contain a double bond and a singly substi-  
21 tuted succinic anhydride group. The copolymers of the  
22 present invention differ from the PIBSAs prepared by the  
23 chlorination process, since those products contain a double  
24 bond, a ring, other than a succinic anhydride ring or one or  
25 more chlorine atoms.

26

27 The copolymers of the present invention contain no double  
28 bonds, rings, other than succinic anhydride rings, or  
29 chlorine atoms. In addition, the succinic anhydride groups  
30 are doubly substituted (i.e., have two substituents, one of  
31 which may be hydrogen) at the 2- and 3-positions, that is:

32

33

34

14

01

02

03

04

05

06

07

08

09

10

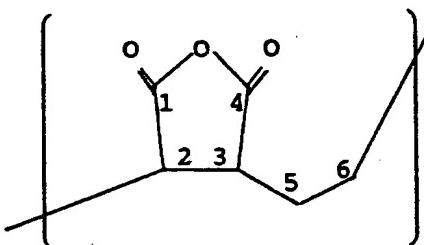
11

The high molecular weight polyalkyl group is derived from a high molecular weight olefin. The high molecular weight olefins used in the preparation of the copolymers of the present invention are of sufficiently long chain length so that the resulting composition is soluble in and compatible with mineral oils, fuels and the like; and the alkylvinylidene isomer of the high molecular weight olefin comprises at least about 20% of the total olefin composition.

19

20

Such high molecular weight olefins are generally mixtures of molecules having different molecular weights and can have at least one branch per 6 carbon atoms along the chain, preferably at least one branch per 4 carbon atoms along the chain, and particularly preferred that there be about one branch per 2 carbon atoms along the chain. These branched chain olefins may conveniently comprise polyalkenes prepared by the polymerization of olefins of from 3 to 6 carbon atoms, and preferably from olefins of from 3 to 4 carbon atoms, and more preferably from propylene or isobutylene. The addition-polymerizable olefins employed are normally 1-olefins. The branch may be of from 1 to 4 carbon atoms, more usually of from 1 to 2 carbon atoms and preferably methyl.



#### A(1) High Molecular Weight Polyalkylene Group

15

01 The preferred alkylvinylidene isomer comprises a methyl- or  
02 ethylvinylidene isomer, more preferably the methylvinylidene  
03 isomer.

04

05 The especially preferred high molecular weight olefins used  
06 to prepare the copolymers of the present invention are poly-  
07 isobutenes which comprise at least about 20% of the more  
08 reactive methylvinylidene isomer, preferably at least 50%  
09 and more preferably at least 70%. Suitable polyisobutenes  
10 include those prepared using  $\text{BF}_3$  catalysis. The preparation  
11 of such polyisobutenes in which the methylvinylidene isomer  
12 comprises a high percentage of the total composition is  
13 described in U.S. Patents Nos. 4,152,499 and 4,605,808.

14

Polyisobutenes produced by conventional  $\text{AlCl}_3$  catalysis when reacted with unsaturated acidic reactants, such as maleic anhydride, in the presence of a free radical initiator, produce products similar to thermal PIBSA in molecular weight and thus do not produce a copolymeric product.

ט

Preferred are polyisobutenes having average molecular weights of about 500 to about 5000. Especially preferred are those having average molecular weights of about 900 to about 2500.

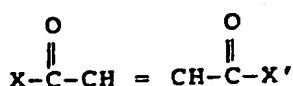
25

### A(2) Unsaturated Acidic Reactant

27

28 The unsaturated acidic reactant used in the preparation of  
29 the copolymers of the present invention comprises a maleic  
30 or fumaric reactant of the general formula:

31



01 wherein X and X' are the same or different, provided that at  
02 least one of X and X' is a group that is capable of reacting  
03 to esterify alcohols, form amides or amine salts with ammo-  
04 nia or amines, form metal salts with reactive metals or  
05 basically reacting metal compounds and otherwise function to  
06 acylate. Typically, X and/or X' is -OH, -O-hydrocarbyl,  
07 -OM<sup>+</sup> where M<sup>+</sup> represents one equivalent of a metal, ammonium  
08 or amine cation, -NH<sub>2</sub>, -Cl, -Br, and taken together X and X'  
09 can be -O- so as to form an anhydride. Preferably, X and X'  
10 are such that both carboxylic functions can enter into  
11 acylation reactions. Preferred are acidic reactants where X  
12 and X' are each independently selected from the group con-  
13 sisting of -OH, -Cl, -O- lower alkyl and when taken  
14 together, X and X' are -O-. Maleic anhydride is the pre-  
15 fered acidic reactant. Other suitable acidic reactants  
16 include electron-deficient olefins such as monophenyl maleic  
17 anhydride; monomethyl, dimethyl, monochloro, monobromo,  
18 monofluoro, dichloro and difluoro maleic anhydride; N-phenyl  
19 maleimide and other substituted maleimides; isomaleimides;  
20 fumaric acid, maleic acid, alkyl hydrogen maleates and  
21 fumarates, dialkyl fumarates and maleates, fumaronilic acids  
22 and maleanic acids; and maleonitrile, and fumaronitrile.  
23  
24 Preferred unsaturated acidic reactants include maleic  
25 anhydride, and maleic acid. The particularly preferred  
26 acidic reactant is maleic anhydride.

27

A(3) General Preparation of Copolymer

29

30 As noted above, the copolymers of the present invention are  
31 prepared by reacting a reactive high molecular weight olefin  
32 and an unsaturated acidic reactant in the presence of a free  
33 radical initiator.

34

01 The reaction may be conducted at a temperature of about  
02 -30°C to about 210°C, preferably from about 40°C to about  
03 150°C. I have found that degree of polymerization is  
04 inversely proportional to temperature. Accordingly, for the  
05 preferred high molecular weight copolymers, it is advan-  
06 tageous to employ lower reaction temperatures. For example,  
07 if the reaction is conducted at about 138°C, an average  
08 degree of polymerization of about 1.3 was obtained. How-  
09 ever, if the reaction was conducted at a temperature of  
10 about 40°C, an average degree of polymerization of about  
11 10.5 was obtained.

12  
13 The reaction may be conducted neat, that is, both the high  
14 molecular weight olefin, and acidic reactant and the free  
15 radical initiator are combined in the proper ratio, and then  
16 stirred at the reaction temperature.

17  
18 Alternatively, the reaction may be conducted in a diluent.  
19 For example, the reactants may be combined in a solvent.  
20 Suitable solvents include those in which the reactants and  
21 free radical initiator are soluble and include acetone,  
22 tetrahydrofuran, chloroform, methylene chloride, dichloro-  
23 ethane, toluene, dioxane, chlorobenzene, xylenes, or the  
24 like. After the reaction is complete, volatile components  
25 may be stripped off. When a diluent is employed, it is  
26 preferably inert to the reactants and products formed and is  
27 generally used in an amount sufficient to ensure efficient  
28 stirring.

29  
30 Moreover, my colleague W. R. Ruhe, has discovered that in  
31 the preparation of polyPIBSA, improved results are obtained  
32 by using PIBSA or polyPIBSA as a solvent for the reaction.  
33 (See, e.g., Examples 16, 17A and 17B herein.)

34

01 In general, the copolymerization can be initiated by any  
02 free radical initiator. Such initiators are well known in  
03 the art. However, the choice of free radical initiator may  
04 be influenced by the reaction temperature employed.

05  
06 The preferred free-radical initiators are the peroxide-type  
07 polymerization initiators and the azo-type polymerization  
08 initiators. Radiation can also be used to initiate the  
09 reaction, if desired.

10  
11 The peroxide-type free-radical initiator can be organic or  
12 inorganic, the organic having the general formula:  $R_3OOR'_3$ ,  
13 where  $R_3$  is any organic radical and  $R'_3$  is selected from the  
14 group consisting of hydrogen and any organic radical. Both  
15  $R_3$  and  $R'_3$  can be organic radicals, preferably hydrocarbon,  
16 aroyl, and acyl radicals, carrying, if desired, substituents  
17 such as nitrogens, etc. Preferred peroxides include  
18 di-tert-butyl peroxide, tert-butyl peroxybenzoate, and  
19 dicumyl peroxide.

20  
21 Examples of other suitable peroxides, which in no way are  
22 limiting, include benzoyl peroxide; lauroyl peroxide; other  
23 tertiary butyl peroxides; 2,4-dichlorobenzoyl peroxide;  
24 tertiary butyl hydroperoxide; cumene hydroperoxide; diacetyl  
25 peroxide; acetyl hydroperoxide; diethylperoxycarbonate;  
26 tertiary butyl perbenzoate; and the like.

27  
28 The azo-type compounds, typified by alpha,alpha'-azo-  
29 bis(isobutyronitrile, are also well-known free-radical  
30 promoting materials. These azo compounds can be defined as  
31 those having present in the molecule group -N=N wherein the  
32 balances are satisfied by organic radicals, at least one of  
33 which is preferably attached to a tertiary carbon. Other  
34 suitable azo compounds include, but are not limited to,

01 p-bromobenzenediazonium fluoborate; p-tolyldiazoaminoben-  
02 zene; p-bromobenzenediazonium hydroxide; azomethane and  
03 phenyldiazonium halides. A suitable list of azo-type com-  
04 pounds can be found in U.S. Patent No. 2,551,813, issued  
05 May 8, 1951 to Paul Pinkney.

06  
07 The amount of initiator to employ, exclusive of radiation,  
08 of course, depends to a large extent on the particular  
09 initiator chose, the high molecular olefin used and the  
10 reaction conditions. The initiator must, of course, be  
11 soluble in the reaction medium. The usual concentrations of  
12 initiator are between 0.001:1 and 0.2:1 moles of initiator  
13 per mole of acidic reactant, with preferred amounts between  
14 0.005:1 and 0.10:1.

15  
16 The polymerization temperature must be sufficiently high to  
17 ~~allow down the initiation to produce the desired copolymer~~  
18 cals. For example, using benzoyl peroxide as the initiator,  
19 the reaction temperature can be between about 75°C and about  
20 90°C, preferably between about 80°C and about 85°C. Higher  
21 and lower temperatures can be employed, a suitable broad  
22 range of temperatures being between about 20°C and about  
23 200°C, with preferred temperatures between about 50°C and  
24 about 150°C.

25  
26 The reaction pressure should be sufficient to maintain the  
27 solvent in the liquid phase. Pressures can therefore vary  
28 between about atmospheric and 100 psig or higher, but the  
29 preferred pressure is atmospheric.

30  
31 The reaction time is usually sufficient to result in the  
32 substantially complete conversion of the acidic reactant and  
33 high molecular weight olefin to copolymer. The reaction  
34

20

01 time is suitable between one and 24 hours, with preferred  
02 reaction times between two and ten hours.

03

04 As noted above, the subject reaction is a solution-type  
05 polymerization reaction. The high molecular weight olefin,  
06 acidic reactant, solvent and initiator can be brought  
07 together in any suitable manner. The important factors are  
08 intimate contact of the high molecular weight olefin and  
09 acidic reactant in the presence of a free-radical producing  
10 material. The reaction, for example, can be conducted in a  
11 batch system where the high molecular weight olefin is added  
12 all initially to a mixture of acidic reactant, initiator and  
13 solvent or the high molecular weight olefin can be added  
14 intermittently or continuously to the reaction pot. Alter-  
15 natively, the reactants may be combined in other orders; for  
16 example, acidic reactant and initiator may be added to high  
17 another manner, the components in the reaction mixture can  
18 be added continuously to a stirred reactor with continuous  
19 removal of a portion of the product to a recovery train or  
20 to other reactors in series. The reaction can also suit-  
21 ably take place in a coil-type reactor where the components  
22 are added at one or more points along the coil.

24

25 In one envisioned embodiment, the reaction product of an  
26 unsaturated acidic reactant and a high molecular weight,  
27 high vinylidene-containing olefin is further reacted  
28 thermally. In this embodiment, any unreacted olefin,  
29 generally the more hindered olefins, i.e., the non-vinyl-  
30 idene, that do not react readily with the unsaturated acidic  
31 reactant under free radical conditions are reacted with  
32 unsaturated acidic reactant under thermal conditions, i.e.,  
33 at temperatures of about 180° to 280°C. These conditions

34

21

01 are similar to those used for preparing thermal process  
02 PIBSA.

03

04 The reaction solvent, as noted above, must be one which  
05 dissolves both the acidic reactant and the high molecular  
06 weight olefin. It is necessary to dissolve the acidic  
07 reactant and high molecular weight olefin so as to bring  
08 them into intimate contact in the solution polymerization  
09 reaction. It has been found that the solvent must also be  
10 one in which the resultant copolymers are soluble.

11

12 Suitable solvents include liquid saturated or aromatic  
13 hydrocarbons having from six to 20 carbon atoms; ketones  
14 having from three to five carbon atoms; and liquid saturated  
15 aliphatic dihalogenated hydrocarbons having from one to five  
16 carbon atoms per molecule, preferably from one to three car-  
17 bon atoms per molecule. By "molecule" is meant "mole" under  
18 the conditions of polymerization. In the dihalogenated  
19 hydrocarbons, the halogens are preferably on adjacent carbon  
20 atoms. By "halogen" is meant F, Cl and Br. The amount of  
21 solvent must be such that it can dissolve the acidic reac-  
22 tant and high molecular weight olefin in addition to the  
23 resulting copolymers. The volume ratio of solvent to high  
24 molecular weight olefin is suitably between 1:1 and 100:1  
25 and is preferably between 1.5:1 and 4:1.

26

27 Suitable solvents include the ketones having from three to  
28 six carbon atoms and the saturated dichlorinated hydro-  
29 carbons having from one to five, more preferably one to  
30 three, carbon atoms.

31

32 Examples of suitable solvents include, but are not limited  
33 to:  
34

22

- 01 1. ketones, such as: acetone; methylethylketone;  
02 diethylketone; and methylisobutylketone;  
03  
04 2. aromatic hydrocarbons, such as: benzene; xylene; and  
05 toluene;  
06  
07 3. saturated dihalogenated hydrocarbons, such as:  
08 dichloromethane; dibromomethane; 1-bromo-2-chloroethane;  
09 1,1-dibromoethane; 1,1-dichloroethane;  
10 1,2-dichloroethane; 1,3-dibromopropane;  
11 1,2-dibromopropane; 1,2-dibromo-2-methylpropane;  
12 1,2-dichloropropane; 1,1-dichloropropane;  
13 1,3-dichloropropane; 1-bromo-2-chloropropane;  
14 1,2-dichlorobutane; 1,5-dibromopentane; and  
15 1,5-dichloropentane; or  
16  
17 .. mixtures of the above, such as: benzene-  
18 methylethylketone.  
19  
20 As noted previously, W. K. Suhe has discovered that use of a  
21 mixture of copolymer and polyisobutene as a solvent results  
22 in improved yields and advantageously dissolves the acidic  
23 reactant when used as a reaction medium.  
24  
25 The copolymer is conveniently separated from solvent and  
26 unreacted acidic reactant by conventional procedures such as  
27 phase separation, solvent distillation, precipitation and  
28 the like. If desired, dispersing agents and/or cosolvents  
29 may be used during the reaction.  
30  
31 The isolated copolymer may then be reacted with a polyamine  
32 to form a polymeric succinimide. The preparation and  
33  
34

23

01 characterization of such polysuccinimides and their treat-  
02 ment with other agents to give other dispersant compositions  
03 is described herein.

04

05 A(4) Preferred Copolymers

06

07 Preferred copolymers include those where an unsaturated  
08 acidic reactant, most preferably maleic anhydride, is  
09 copolymerized with a "reactive" polyisobutene, in which at  
10 least about 50 percent or more of the polyisobutene com-  
11 prises the alkylvinylidene, more preferably, the methyl-  
12 vinylidene, isomer, to give a "polyPIBSA".

13

14 Preferred are polyPIBSAs wherein the polyisobutyl group has  
15 an average molecular weight of about 500 to about 5000, more  
16 preferably from about 950 to about 2500. Preferred are  
17 polyPIBSAs having an average degree of polymerization of  
18 about 1.1 to about 20, more preferably from about 1.5 to  
19 about 10.

20

21 B. POLYSUCCINIMIDES

22

23 The polyamino polysuccinimides of the present invention are  
24 prepared by reacting a copolymer of the present invention  
25 with a polyamine. Polysuccinimides which may be prepared  
26 include monopolysuccinimides (where a polyamine component  
27 reacts with one succinic group), bis-polysuccinimides (where  
28 a polyamine component reacts with a succinic group from each  
29 of two copolymer molecules), higher succinimides (where a  
30 polyamine component reacts with a succinic group from each  
31 of more than 2 copolymer molecules) or mixtures thereof.

32 The polysuccinimide(s) produced may depend on the charge  
33 mole ratio of polyamine to succinic groups in the copolymer  
34 molecule and the particular polyamine used. Using a charge

24

01 mole ratio of polyamine to succinic groups in copolymer of  
02 about 1.0, predominately monopolysuccinimide is obtained.  
03 Charge mole ratios of polyamine to succinic group in copoly-  
04 mer of about 1:2 may produce predominately bis-polysucci-  
05 nimide. Higher polysuccinimides may be produced if there is  
06 branching in the polyamine so that it may react with a  
07 succinic group from each of greater than 2 copolymer  
08 molecules.

09

10 B(1) Preferred Copolymers

11

12 Preferred copolymers include polyPIBSAs prepared according  
13 to the present invention as described hereinabove.

14

15 Preferred polyPIBSAs include those prepared using a poly-  
16 isobutene of average molecular weight of about 500 to about  
17 5000, preferably of about 950 to about 2500 and wherein at  
18 least about 50 percent of the total polyisobutene comprises  
19 the alkylvinylidene isomer. Preferred alkylvinylidene  
20 isomers include methylvinylidene and ethylvinylidene.  
21 Especially preferred is methylvinylidene. Preferred are  
22 polyPIBSAs having an average degree of polymerization of  
23 about 1.1 to about 15. Particularly preferred polyPIBSAs  
24 have an average degree of polymerization of about 1.5 to  
25 about 10, and which are prepared using a polyisobutene  
26 having an average molecular weight of about 900 to about  
27 2500.

28

29 B(2) Polyamine

30

31 The polyamine employed to prepare the polyamino poly-  
32 succinimides is preferably polyamine having from 2 to about  
33 12 amine nitrogen atoms and from 2 to about 40 carbon atoms.  
34 The polyamine is reacted with polyPIBSA to produce the poly-

35

01 amino polysuccinimide, employed in this invention. The  
02 polyamine is so selected so as to provide at least one basic  
03 amine per succinimide group. Since the reaction of a  
04 nitrogen of a polyamino polysuccinimide to form a hydro-  
05 carbonyl oxycarbonyl, a hydroxy hydrocarbyl oxycarbonyl or a  
06 hydroxy polyoxyalkylene oxycarbonyl is believed to effi-  
07 ciently proceed through a secondary or primary amine, at  
08 least one of the basic amine atoms of the polyamino poly-  
09 succinimide must either be a primary amine or a secondary  
10 amine. Accordingly, in those instances in which the  
11 succinimide group contains only one basic amine, that amine  
12 must either be a primary amine or a secondary amine. The  
13 polyamine preferably has a carbon-to-nitrogen ratio of from  
14 about 1:1 to about 10:1.

15 The polyamine portion of the polyamino polysuccinimide may  
16 be substituted with substituents selected from (a) hydrocarbyl  
17 (b) hydrocarbyl groups of from 1 to about 10 carbon atoms,  
18 (c) acyl groups of from 2 to about 10 carbon atoms, and  
19 (d) monoketo, monohydroxy, mononitro, monocyan, lower alkyl  
20 and lower alkoxy derivatives of (b) and (c). "Lower", as  
21 used in terms like "lower alkyl" or "lower alkoxy", means a  
22 group containing from 1 to about 6 carbon atoms. At least  
23 one of the substituents on one of the amines of the  
24 polyamine is hydrogen, e.g., at least one of the basic  
25 nitrogen atoms of the polyamine is a primary or secondary  
26 amino nitrogen atom.

28       Hydrocarbyl, as used in describing the polyamine components  
29       of this invention, denotes an organic radical composed of  
30       carbon and hydrogen which may be aliphatic, alicyclic,  
31       aromatic or combinations thereof, e.g., aralkyl. Prefer-  
32       ably, the hydrocarbyl group will be relatively free of  
33       aliphatic unsaturation, i.e., ethylenic and acetylenic,  
34

26

01 particularly acetylenic unsaturation. The substituted  
02 polyamines of the present invention are generally, but not  
03 necessarily, N-substituted polyamines. Exemplary hydro-  
04 carbyl groups and substituted hydrocarbyl groups include  
05 alkyls such as methyl, ethyl, propyl, butyl, isobutyl,  
06 pentyl, hexyl, octyl, etc., alkenyls such as propenyl,  
07 isobutenyl, hexenyl, octenyl, etc., hydroxyalkyls, such as  
08 2-hydroxyethyl, 3-hydroxypropyl, hydroxyisopropyl,  
09 4-hydroxybutyl, etc. ketoalkyls, such as 2-ketopropyl,  
10 6-ketoctyl, etc., alkoxy and lower alenoxy alkyls, such as  
11 ethoxyethyl, ethoxypropyl, propoxyethyl, propoxypropyl,  
12 2-(2-ethoxyethoxy)ethyl, 2-(2-(2-ethoxyethoxy)ethoxy)ethyl,  
13 3,6,9,12-tetraoxatetradecyl, 2-(2-ethoxyethoxy)hexyl, etc.  
14 The acyl groups of the aforementioned (c) substituents are  
15 such as propionyl, acetyl, etc. The more preferred substit-  
16 uents are hydrogen, C<sub>1</sub>-C<sub>6</sub> alkyls and C<sub>1</sub>-C<sub>6</sub> hydroxyalkyls.

17 In a substituted polyamine the substituents are found at any  
18 atom capable of receiving them. The substituted atoms,  
19 e.g., substituted nitrogen atoms, are generally geometri-  
20 cally inequivalent, and consequently the substituted amines  
21 finding use in the present invention can be mixtures of  
22 mono- and polysubstituted polyamines with substituent groups  
23 situated at equivalent and/or inequivalent atoms.

25 The more preferred polyamine finding use within the scope of  
26 the present invention is a polyalkylene polyamine, including  
27 alkylene diamine, and including substituted polyamines,  
28 e.g., alkyl substituted polyalkylene polyamine. Preferably,  
29 the alkylene group contains from 2 to 6 carbon atoms, there  
30 being preferably from 2 to 3 carbon atoms between the  
31 nitrogen atoms. Such groups are exemplified by ethylene,  
32 1,2-propylene, 2,2-dimethylpropylene, trimethylene, etc.  
33 Examples of such polyamines include ethylene diamine,

27

01 diethylene triamine, di(trimethylene)triamine, dipropylene  
02 triamine, triethylene tetramine, tripropylene tetramine,  
03 tetraethylene pentamine, and pentaethylene hexamine. Such  
04 amines encompass isomers such as branched-chain polyamine  
05 and the previously mentioned substituted polyamines,  
06 including hydrocarbyl-substituted polyamines. Among the  
07 polyalkylene polyamines, those containing 2-12 amine  
08 nitrogen atoms and 2-24 carbon atoms are especially  
09 preferred, and the C<sub>2</sub>-C<sub>5</sub> alkylene polyamines are most  
10 preferred, in particular, the lower polyalkylene polyamines,  
11 e.g., ethylene diamine, dipropylene triamine, etc.

12  
13 Preferred polyamines also include heavy polyamines such as  
14 polyamine HPA available from Union Carbide.

15  
16 The polyamine component also may contain heterocyclic poly-  
17 -amino-, heterocyclic substituted amines and substituted  
18 heterocyclic compounds, wherein the heterocycle comprises  
19 one or more 5 to 6-membered rings containing oxygen and/or  
20 nitrogen. Such heterocycles may be saturated or unsaturated  
21 and substituted with groups selected from the aforementioned  
22 (a), (b), (c) and (d). The heterocycles are exemplified by  
23 piperazines, such as 2-methylpiperazine, N-(2-hydroxyethyl)-  
24 piperazine, 1,2-bis-(n-piperazinyl)ethane, and N,N'-bis(N-  
25 piperazinyl)piperazine, 2-methylimidazoline, 3-amino-  
26 piperidine, 2-aminopyridine, 2-(3-aminoethyl)-3-pyrroline,  
27 3-aminopyrrolidine, N-(3-aminopropyl)-morpholine, etc.  
28 Among the heterocyclic compounds, the piperazines are  
29 preferred.

30  
31 Typical polyamines that can be used to form the compounds of  
32 this invention include the following:

33  
34

28

01 ethylene diamine, 1,2-propylene diamine, 1,3-propylene  
02 diamine, diethylene triamine, triethylene tetramine,  
03 hexamethylene diamine, tetraethylene pentamine, methyl-  
04 aminopropylene diamine, N-(betaaminoethyl)piperazine,  
05 N,N'-di(betaaminoethyl)piperazine, N,N'-di(beta-amino-  
06 ethyl)-imidazolidone-2, N-(beta-cyanoethyl)ethane-1,2-  
07 diamine, 1,3,6,9-tetraaminooctadecane, 1,3,6-triamino-9-  
08 oxadecane, N-(beta-aminoethyl)diethanolamine, N-methyl-1,2-  
09 propanediamine, 2-(2-aminoethylamino)-ethanol, 2-[2-(2-amino-  
10 ethylamino)ethylamino]-ethanol.

11

12 Another group of suitable polyamines are the propylene-  
13 amines, (bisaminopropylethylenediamines). Propyleneamines  
14 are prepared by the reaction of acrylonitrile with an  
15 ethyleneamine, for example, an ethyleneamine having the  
16 formula  $H_2N(CH_2CH_2NH)_jH$  wherein  $j$  is an integer from 1 to 5,  
17 followed by  $\text{H}_2\text{N}(\text{CH}_2)_j\text{NH}(\text{CH}_2)_j\text{NH}_2$  as the resultant intermediate.  
18 Thus, the product prepared from ethylene diamine and  
19 acrylonitrile would be  $H_2N(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$ .  
20

21 In many instances the polyamine used as a reactant in the  
22 production of polysuccinimides of the present invention is  
23 not a single compound but a mixture in which one or several  
24 compounds predominate with the average composition indi-  
25 cated. For example, tetraethylene pentamine prepared by the  
26 polymerization of aziridine or the reaction of dichloro-  
27 ethylene and ammonia will have both lower and higher amine  
28 members, e.g., triethylene tetramine, substituted  
29 piperazines and pentaethylene hexamine, but the composition  
30 will be largely tetraethylene pentamine and the empirical  
31 formula of the total amine composition will closely  
32 approximate that of tetraethylene pentamine. Finally, in  
33 preparing the polysuccinimide for use in this invention,  
34 where the various nitrogen atoms of the polyamine are not

29

01 geometrically equivalent, several substitutional isomers are  
02 possible and are encompassed within the final product.  
03 Methods of preparation of polyamines and their reactions are  
04 detailed in Sidgewick's "The Organic Chemistry of Nitrogen",  
05 Clarendon Press, Oxford, 1966; Noller's "Chemistry of  
06 Organic Compounds", Saunders, Philadelphia, 2nd Ed., 1957;  
07 and Kirk-Othmer's "Encyclopedia of Chemical Technology", 2nd  
08 Ed., especially Volume 2, pp. 99-116.

09

10

B(3) General Preparation

11

12 The polysuccinimides are prepared by reacting copolymer with  
13 a polyamine to form a mono-, bis-polysuccinimide, higher  
14 polysuccinimide or mixtures thereof. The charge mole ratio  
15 of polyamine to succinic groups in copolymer may determine  
16 the mixture of polysuccinimides formed. For example, a  
17 product comprising mono-, bis-polysuccinimide or higher  
18 polysuccinimide can be prepared by controlling the molar  
19 ratios of the polyamine and succinic groups in copolymer and  
20 the polyamine used. Thus, if about one mole of polyamine is  
21 reacted with one mole of succinic group in the copolymer, a  
22 predominately mono-polysuccinimide product will be prepared.  
23 If about two moles of succinic group in the copolymer are  
24 reacted per mole of polyamine, a bis-polysuccinimide may be  
25 prepared. If higher amounts of succinic group in copolymer  
26 are used, higher polysuccinimides may be prepared provided  
27 that there are sufficient basic amino groups (or sufficient  
28 branching) in the polyamine to react with a succinic group  
29 from each of several copolymer molecules to produce the  
30 higher polysuccinimide. Due to the cross-linking of  
31 copolymer molecules by the polyamine component, compositions  
32 of very high molecular weight, on the order of about 10,000  
33 to about 100,000 may be prepared.

34

30

01 The reaction of a polyamine with an alkenyl or alkyl  
02 succinic anhydride to produce the polyamino alkenyl or alkyl  
03 succinimides is well known in the art and is disclosed in  
04 U.S. Patents Nos. 2,992,708; 3,018,291; 3,024,237;  
05 3,100,673; 3,219,666; 3,172,892; and 3,272,746. The above  
06 are incorporated herein by reference for their disclosures  
07 of preparing alkenyl or alkyl succinimides. The present  
08 polysuccinimides may be prepared by following the general  
09 procedures described therein.

10  
11 Accordingly, polyamine and copolymer are contacted at the  
12 desired molar ratio to give the desired mono-, bispoly-  
13 succinimides or higher polysuccinimides or mixtures thereof.  
14 The reaction may be carried out neat or preferably in  
15 solution. Suitable solvents include organic solvents,  
16 including alcohols, aliphatic and aromatic solvents, and the  
17 like. The reaction is conducted at a temperature of about  
18 80°C to about 250°C, preferably from about 120°C to about  
19 180°C and is generally complete within about 2 to about 24  
20 hours. The reaction may be conducted under ambient pressure  
21 and atmospheric conditions, although a nitrogen atmosphere  
22 at atmospheric pressure may be preferred. The desired  
23 product may be isolated by conventional procedures, such as  
24 water wash and stripping, usually with the aid of vacuum, of  
25 any residual solvent.

26  
27       B(4) General Preparation of Preferred Polysuccinimides  
28

29 The preferred polysuccinimides of the present invention are  
30 prepared by reacting a polyPIBSA copolymer of the present  
31 invention with polyamine. The charge mole ratio of  
32 polyamine to succinic groups in the polyPIBSA will effect  
33 whether monopolysuccinimides, bis-polysuccinimides, or  
34 higher polysuccinimides or mixtures thereof are produced

31

01 and/or predominate. Accordingly, with a charge mole ratio  
02 (CMR) of about one mole of polyamine per mole of succinic  
03 groups in the polyPIBSA primarily mono-polysuccinimide will  
04 be formed. However, at a CMR of 0.5 mole polyamine per mole  
05 of succinic group in the polyPIBSA, there is a tendency to  
06 form bis-polysuccinimides where the polyamine component acts  
07 to link two succinic groups, thusly forming a cross-linked  
08 composition. Accordingly, the reaction of polyPIBSA and  
09 polyamine will yield a mixture of products which I term  
10 "polysuccinimides" and which term includes monopolysuccini-  
11 mides, also higher succinimides and bis-polysuccinimides and  
12 compositions of intermediate structure.

13

14 The reaction is carried out by contacting polyamine and  
15 polyPIBSA. Although the ratio of the reactants is not  
16 critical, as noted above a CMR may be chosen so as to yield  
17 desired polysuccinimide proportions. The reaction is  
18 carried out at a temperature sufficient to cause reaction of  
19 the polyamine with a succinic group of the polyPIBSA. In  
20 particular, reaction temperatures from about 140°C to about  
21 180°C are preferred, with temperatures from about 140°C to  
22 about 170°C being especially preferred.

23

24 The reaction may be conducted neat - that is both the  
25 polyamine and the polyPIBSA are combined and then stirred at  
26 the reaction temperature.

27

28 Alternatively, the reaction may be conducted in a diluent.  
29 For example, the reactants may be combined in a solvent such  
30 as aliphatic or aromatic solvents, and the like, and then  
31 stirred at the reaction temperature. After completion of  
32 the reaction, volatile components may be stripped off. When

33

34

32

01 a diluent is employed, it is preferably inert to the reac-  
02 tants and products formed and is generally used in an amount  
03 sufficient to ensure efficient stirring.

04

05 Preferred are polyamines having from about 2 to about 12  
06 amine nitrogen atoms and from about 2 to about 40 carbon  
07 atoms. The more preferred polyamines employed in this  
08 reaction are generally represented by the formula:

09



11

12 wherein Y is an alkylene group of 2 to 10 carbon atoms,  
13 preferably from 2 to 6 carbon atoms, and a is an integer  
14 from about 1 to 11, preferably from 1 to 6. However, the  
15 preparation of these alkylene polyamines does not produce a  
16 single compound and cyclic heterocycles, such as piperazine,  
17 may be formed to some extent in the alkylene diamines.

18

19                           B(5) Preferred Polysuccinimides

20

21                           (a) Monopolysuccinimides

22 Preferred monopolysuccinimides include those having the  
23 following formula:

24

25

26

27

28

29

30

31

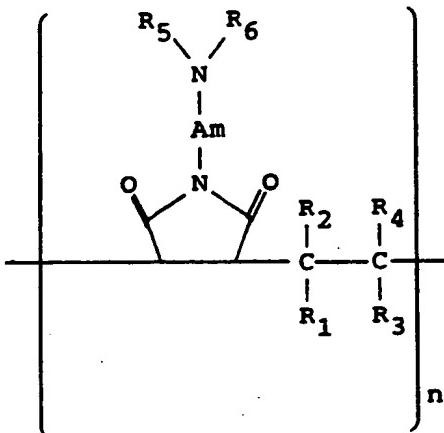
32

33

34

33

01  
02  
03  
04  
05  
06  
07  
08  
09  
10  
11  
12



13 wherein Am is a linking group having from about 0 to about  
14 10 amine nitrogen atoms and from about 2 to about 40 carbon  
15 atoms; n is 1 or greater and R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are selected  
16 from hydrogen lower alkyl of 1 to 6 carbon atoms; and high  
17 molecular weight polyalkyl; wherein either R<sub>1</sub> and R<sub>2</sub> are  
18 hydrogen and one of R<sub>3</sub> and R<sub>4</sub> is lower alkyl and the other  
19 is high molecular weight polyalkyl or R<sub>3</sub> and R<sub>4</sub> are hydrogen  
20 and one of R<sub>1</sub> and R<sub>2</sub> is lower alkyl and the other is high  
21 molecular weight polyalkyl; and R<sub>5</sub> and R<sub>6</sub> are independently  
22 hydrogen, lower alkyl of 1 to 6 carbon atoms, phenyl or  
23 taken together are alkylene of 3 to 6 carbon atoms to give a  
24 ring.

25

26 Preferred high molecular weight polyalkyl groups include  
27 polyisobutyl groups having at least about 30 carbon atoms,  
28 more preferably, at least about 50 carbon atoms. Especially  
29 preferred are polyisobutyl groups having an average  
30 molecular weight of about 500 to about 5000, more preferably  
31 from about 900 to about 2500.

32

33

34

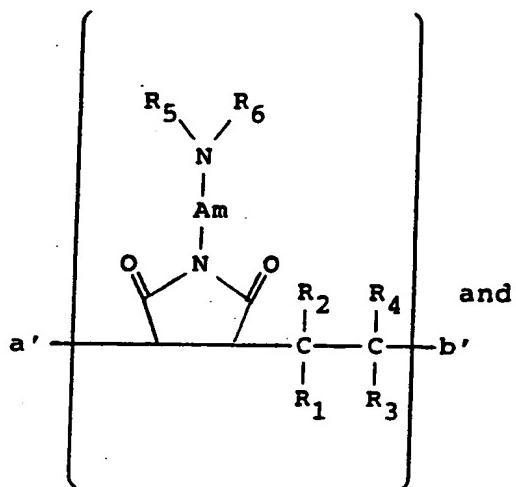
34

- 01 Preferred lower alkyl groups include methyl and ethyl.
- 02 Especially preferred are compounds where the lower alkyl group is methyl.
- 04
- 05 Preferred are compounds where R<sub>5</sub> and R<sub>6</sub> are hydrogen or
- 06 methyl; preferred R<sub>5</sub> and R<sub>6</sub> groups include hydrogen.
- 07
- 08 Preferred are Am groups having from about 0 to about 10
- 09 amine nitrogen atoms and from about 2 to about 40 carbon
- 10 atoms. More preferred are Am groups of the formula
- 11 -[(ZNH)<sub>p</sub>Z']- wherein Z and Z' are independently alkylene of
- 12 from about 2 to about 6 carbon atoms and p is an integer
- 13 from 1 to 6. Especially preferred are Am groups where Z and
- 14 Z' are ethylene and p is 2, 3 or 4.
- 15
- 16 Preferred are compounds where n is from about 2 to about 20,
- 17 more preferably from about 2 to about 10.
- 18
- 19 Preferred are compounds having an average degree of polymer-
- 20 ization of from about 1.1 to about 20, more preferably from
- 21 about 1.5 to about 10.
- 22
- 23 (b) Bis-polysuccinimides
- 24
- 25 Preferred polysuccinimides include those which partially
- 26 comprise at least in part a bis-polysuccinimide structure.
- 27 Some of these preferred polysuccinimides are random poly-
- 28 succinimides which comprise units selected from:
- 29
- 30
- 31
- 32
- 33
- 34

35

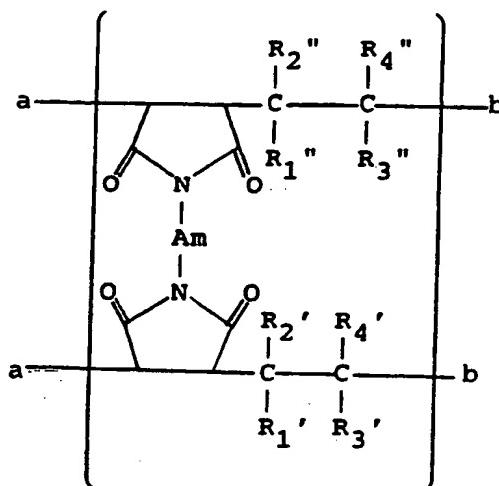
01  
02  
03  
04  
05  
06  
07  
08  
09  
10  
11  
12  
13  
14

A



and

B



15 wherein Am is a linking group having from about 0 to 10  
 16 amine nitrogen atoms and from about 2 to 40 carbon atoms;  
 17 -  
 18  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_1'$ ,  $R_2'$ ,  $R_3'$ ,  $R_4'$ ,  $R_1''$ ,  $R_2''$ ,  $R_3''$ , and  $R_4''$   
 19 are selected from hydrogen, lower alkyl of one to 6 carbon  
 20 atoms and high molecular weight polyalkyl; wherein either  $R_1$   
 21 and  $R_2$  are hydrogen and one of  $R_3$  and  $R_4$  is lower alkyl and  
 22 the other is polyalkyl, or  $R_3$  and  $R_4$  are hydrogen and one of  
 23  $R_1$  and  $R_2$  is lower alkyl and the other is polyalkyl; either  
 24  $R_1'$  and  $R_2'$  are hydrogen and one of  $R_3'$  and  $R_4'$  is lower  
 25 alkyl and the other is polyalkyl, or  $R_3'$  and  $R_4'$  are  
 26 hydrogen and one of  $R_1'$  and  $R_2'$  is lower alkyl and the other  
 27 is polyalkyl; and either  $R_1''$  and  $R_2''$  are hydrogen and one of  
 28  $R_3''$  and  $R_4''$  is lower alkyl and the other is polyalkyl or  $R_3''$   
 29 and  $R_4''$  are hydrogen and one of  $R_1''$  and  $R_2''$  is lower alkyl  
 30 and the other is polyalkyl and  $R_5$  and  $R_6$  are independently  
 31 hydrogen, lower alkyl of 1 to 6 carbon atoms, phenyl or  
 32 taken together are alkylene of 3 to 6 carbon atoms to give a  
 33 ring; a, a', b and b' are sites for a covalent bond provided  
 34 that at least one a or a' site of each unit is covalently  
 bonded to a b or b' site.

01 Preferred polyalkyl groups include polyisobutyl groups  
02 having at least about 30 carbon atoms, more preferably at  
03 least about 50 carbon atoms. Especially preferred are  
04 polyisobutyl groups having an average molecular weight of  
05 about 500 to about 5000, more preferably from about 900 to  
06 about 2500.

07

08 Preferred lower alkyl groups include methyl and ethyl;  
09 especially preferred is ethyl.

10

11 Preferred Am groups include those having the formula  
12  $\{(\text{ZNH})\text{pZ}'\}^n$  - wherein Z and Z' are independently alkylene of 2  
13 to 6 carbon atoms and p is an integer from 0 to 5.  
14 Especially preferred are Am groups wherein Z and Z' are  
15 ethylene and p is 1, 2 or 3.

16

17 Preferred are random polysuccinimides where the average sum  
18 of A and B units is from about 2 to about 50. Preferred are  
19 random polysuccinimides having molecular weights of from  
20 about 10,000 to about 150,000.

21

22 Preferred are compounds in which the bis-succinimide  
23 structure predominates, that is those having more B units  
24 than A units, preferably on the order of about 2 to about 10  
25 times as many B units as A units. Such compounds are  
26 preferred in part due to their high average molecular  
27 weights, on the order of about 10,000 to about 150,000 which  
28 may be related to their exhibiting an advantageous V.I.  
29 credit as well as dispersantability when used in a  
30 lubricating oil composition.

31

32 It is believed that polysuccinimide compounds in which a  
33 significant portion comprises a bis-polysuccinimide  
34 structure (an embodiment which is exemplified in FIG. 1)

01 comprise network or ladder polymers. Such polymers are  
02 cross-linked in an orderly manner. It is believed that this  
03 orderly cross-linking allows for the formation of composi-  
04 tions having very high molecular weights, on the order of  
05 about 10,000 to about 150,000 and also contributes to the  
06 advantageous properties of these compositions including  
07 improved dispersancy and V.I. credit. In addition, due to  
08 the cross-linking of the copolymer molecules by the poly-  
09 amine to form the polysuccinimides of the above-noted  
10 structure, such products are harder to hydrolyze and are  
11 more stable to shear forces than are those polysuccinimides  
12 which do not form the ladder structure.

13

14                   (c) Higher Polysuccinimides

15

16 Higher polysuccinimides are prepared by reacting the copoly-  
17 mers of the present invention with a polyamine having  
18 branching such that it can react with a succinic group from  
19 each of greater than two copolymer molecules. Due to this  
20 crosslinking, it is believed that these higher polysucci-  
21 nimides may have gel-like properties besides the dispersant  
22 properties possessed by the other polysuccinimides.

23

24                   C. POLYAMINO POLYSUCCINIMIDES WHEREIN ONE  
25                   OR MORE OF THE NITROGENS IS SUBSTITUTED  
26                   WITH HYDROCARBYL OXYCARBONYL, HYDROXY HYDROCARBYL  
27                   OXYCARBONYL, OR HYDROXY POLY(OXYALKYLENE)OXYCARBONYL  
28                   OR THE POLYSUCCINIMIDE IS OTHERWISE POST-TREATED

29 Commonly-assigned U.S. Patent No. 4,612,132 discloses poly-  
30 amino alkenyl or alkyl succinimides wherein one or more of  
31 the nitrogens of the polyamino moiety is substituted with a  
32 hydrocarbyl oxy carbonyl, or a hydroxy hydrocarbyl oxy car-  
33 bonyl wherein said hydrocarbyl contains from 1 to about 20  
34 carbon atoms and said hydroxy hydrocarbyl contains from  
about 2 to about 20 carbon atoms which may be prepared by

38

01 reaction with a cyclic carbonate; by reaction with a linear  
02 mono- or polycarbonate; or by reaction with a suitable  
03 chloroformate and hydroxy poly(oxyalkylene)oxycarbonyl which  
04 may be formed by reaction with a suitable chloroformate.  
05 U.S. Patent No. 4,612,132 also discloses processes for the  
06 preparation of such modified polyamino alkenyl or alkyl  
07 succinimides.

08  
09 U.S. Patent No. 4,612,132 also discloses the post-treating  
10 of hydroxyhydrocarbyl carbamates prepared from polyamino  
11 alkenyl or alkyl succinimides with an alkenyl or alkyl  
12 succinic anhydride.

13  
14 In addition, U.S. Patent No. 4,612,132 discloses the reac-  
15 tion of the modified succinimides disclosed therein with  
16 boric acid or similar boron compound to give borated  
17 dispersants. Accordingly, the disclosure of U.S. Patent  
18 No. 4,612,132 is incorporated herein by reference.

19  
20 Commonly assigned U.S. Patent No. 4,585,566 discloses  
21 improved dispersants prepared by reacting other  
22 nitrogen-containing dispersants with cyclic carbonates, the  
23 disclosure of which is incorporated herein by reference.

24  
25 Accordingly, by following the procedures disclosed in U.S.  
26 Patents Nos. 4,612,132 and 4,585,566, modified polysuccini-  
27 mides may be prepared. Thus, the polyamino polysuccinimides  
28 wherein one or more of the nitrogens of the polyamino moiety  
29 is substituted with a hydrocarbyl oxycarbonyl, or a hydroxy  
30 hydrocarbyl oxycarbonyl wherein said hydrocarbyl contains  
31 from 1 to about 20 carbon atoms and said hydroxy hydrocarbyl  
32 contains from 2 to about 20 carbon atoms may be prepared by  
33 reaction with a cyclic carbonate; by reaction with a linear  
34 mono- or poly-carbonate; or by reaction with a suitable

39

01 chloroformate. Hydroxy poly(oxyalkylene) oxy carbonyl may be  
02 formed by reaction with a suitable chloroformate. Also,  
03 hydroxy hydrocarbyl carbamates prepared from the polysucci-  
04 nimides of the present invention may be post-treated with an  
05 alkenyl or alkyl succinic anhydride [or even the copolymers  
06 of the present invention (such as polyPIBSA) according to  
07 the procedures disclosed in U.S. Patents Nos. 4,612,132 and  
08 4,585,566. The products so produced are effective disper-  
09 sant and detergent additives for lubricating oils and for  
10 fuel.

11

12 The polysuccinimides and modified polysuccinimides of this  
13 invention can also be reacted with boric acid or a similar  
14 boron compound to form borated dispersants having utility  
15 within the scope of this invention. In addition to boric  
16 acid (boron acid), examples of suitable boron compounds  
17 include boron oxides, boron halides and esters of boro-  
18 acid. Generally from about 0.1 equivalents to 10 equiva-  
19 lents of boron compound to the polysuccinimide or modified  
20 polysuccinimide may be employed.

21

22 Commonly-assigned U.S. Patent No. 4,615,826 discloses the  
23 treating of a succinimide having at least one basic nitrogen  
24 with a fluorophosphoric acid or ammonium salt thereof to  
25 give a hydrocarbon-soluble fluorophosphoric acid adduct.  
26 Accordingly, the disclosure of U.S. Patent No. 4,615,826 is  
27 incorporated herein by reference.

28

29 By following the disclosure of U.S. Patent No. 4,615,826,  
30 hydrocarbon-soluble fluorophosphoric adducts of the poly-  
31 succinimides of the present invention may be prepared. Such  
32 adducts comprise the reaction product of a polysuccinimide  
33 of the present invention and a fluorophosphoric acid or

34

\*\*\*\*\*  
\* User name: HAGEMAT.USERS.ZDX.BASF\_AG.D Print queue: PAMALI-1-DE/Q49\_C6\_V21  
\* File name:  
\* Directory:  
\* Description: LPT8

14:13:03

05/01/21

\*\*\*\*\*

\*

\* H H A GGG EEEEE M M A TTTTT  
\* H H A A G G E MM MM A A T  
\* H H A A G E M M M A A T  
\* HHHHH A A G GGG EEEE M M M A A T  
\* H H AAAAAA G G E M M AAAAAA T  
\* H H A A G G E M M A A T  
\* H H A A GGGG EEEEE M M A A T  
\*

\*\*\*\*\*

\*

L PPPP TTTTT 888  
L P P T 8 8  
L P P T 8 8  
L PPPP T 888  
L P T 8 8  
L P T 8 8  
LLLLL P T 888

\*\*\*\*\*

**(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES  
PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG**

**(19) Weltorganisation für geistiges Eigentum  
Internationales Büro**



**(43) Internationales Veröffentlichungsdatum  
2. August 2001 (02.08.2001)**

**PCT**

**(10) Internationale Veröffentlichungsnummer  
WO 01/55059 A1**

**(51) Internationale Patentklassifikation<sup>7</sup>:** C06B 47/14, (81) Bestimmungsstaaten (*national*): AU, BR, ZA.  
C08F 8/14, 8/30

**(21) Internationales Aktenzeichen:** PCT/EP01/00220

**(84) Bestimmungsstaaten (*regional*):** europäisches Patent (AT,  
BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,  
NL, PT, SE, TR).

**(22) Internationales Anmelddatum:**

10. Januar 2001 (10.01.2001)

**Veröffentlicht:**

*mit internationalem Recherchenbericht*

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**